The Synthesis and Properties of Liquid Crystal Elastomers

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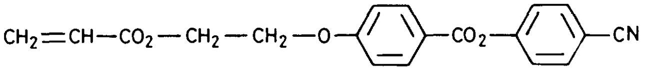
Liquid crystal elastomers have been synthesised in which up to 10 mol% of cross-link units may be introduced without completely disrupting the nematic liquid crystal phase, although the introduction of cross-linking has a marked effect upon the temperatures of the phase transitions.

In recent years considerable interest has been focused on the preparation and properties of polymeric compounds which exhibit thermotropic liquid crystal phases.[1,2] Such materials combine the essential properties of low molar-mass liquid crystals with those of macromolecules. Thus they may show nematic, smectic, and cholesteric phases with the appropriate chemical moieties, but for example, at low temperatures, readily form glasses in which the liquid crystalline structure is 'frozen.' One aspect, which may be of interest in any future application of these materials, is the possibility of forming an elastomeric network with molecules which also exhibit liquid crystal phases.[3] We report here the synthesis and a preliminary study of some of the properties of such liquid crystal elastomers with varying levels of molecular cross-linking.

Acrylate monomers of type (I), in which the mesogenic group is connected to the polymerisable group by a flexible spacer were synthesised using established procedures.[4] Cross-linked polymers were obtained by free-radical polymerisation of a mixture of (I) with diacrylate (II) (where $m = 2$). Typically the monomer mixture and 1% azobisisobutyronitrile were dissolved in chlorobenzene and heated under vacuum at 60 °C for 18 hours. The precipitated polymer was then washed repeatedly with diethyl ether until a fine powder was obtained (with yields typically ~50%). The products were characterised by i.r. and elemental analysis. G.p.c. measurements on the homopolymer of (I) indicated a consistent degree of polymerisation of ~300 with $M_w/M_n \sim 1.8$.



(I)

$CH_2{=}CH{-}CO_2{-}[CH_2]_m{-}O_2C{-}CH{=}CH_2$

(II)

Examination of the samples on a temperature controlled stage using a polarising microscope showed that the lightly cross-linked material exhibited similar behaviour to that observed for a homopolymer of (I). Thus at high temperatures an isotropic phase was formed and on cooling birefringent textures characteristic of a nematic liquid crystal phase were noted. The samples appeared more viscous than the homopolymer and any deformations of the shape of the sample were found to be reversible, consistent with the properties of an elastomer. The highly cross-linked materials did not exhibit a nematic–isotropic phase transition, although some birefringent textures were observed, apparently locked into the glass. Figure 1 shows the phase transition temperatures

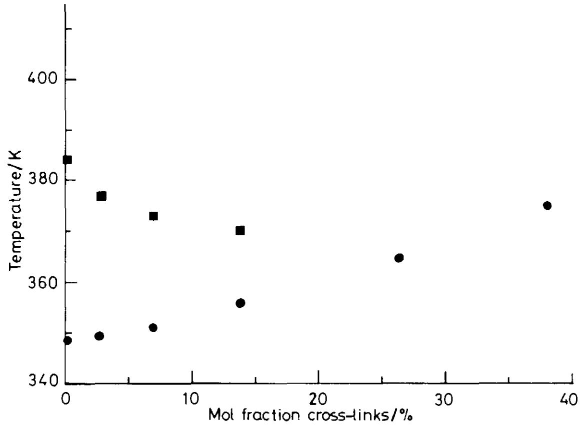


Figure 1. The relationship between the nematic–isotropic transition (■) and the glass transitions (●) as a function of the cross-link density (molar %) in a copolymer formed from (I) & (II) (with $m = 2$). The cross-link density is obtained from the monomer ratios in the feedstock, however see text.

plotted as a function of the degree of cross-linking. These results were obtained using a Perkin–Elmer differential scanning calorimeter DSC-2 with a heating rate of 10 K/min. The increase in the temperature of the glass transition with cross-link density is approximately linear and reflects the increasingly restricted motion available to the polymer chains. For samples of low cross-link density, a nematic–isotropic phase transition is observed; the temperature of this transition is reduced by cross-linking. As a consequence the temperature range of the liquid crystal phase decreases with increasing cross-link density. For the most heavily cross-linked samples therefore, no mobile liquid phase is observed, although in general, these polymers did exhibit birefringent optical textures up to their decomposition point. As inspection of Figure 1 shows, relatively high degrees of cross-linking may be introduced (up to 10% molar concentration) without disrupting the liquid crystal phase. This high level of cross-linking would indicate that molecular motion and hence decoupling of the mesogenic groups *via* the polymer backbone is not an over-riding prerequisite for the formation of a polymeric liquid crystal phase.

The values of cross-link concentration are those obtained from the feedstock ratios. These would only be equivalent to the actual degree of cross-linking if there is random copolymerisation and the reactivities of the two monomers are the same. The former qualification seems most reasonable for free-radical polymerisation. Since the cross-linking unit contains nine bonds the possibility of cyclisation is remote.[5] We have checked the reactivities of the monomer by i.r. and n.m.r. analysis of the fluid in the reaction vessel and of the final products. These would suggest the levels of cross-linking as shown in Figure 1 are close to the actual values (within ±5% of the stated values). These levels of cross-linking are large compared with those normally encountered in conventional elastomers (*i.e.* <1%) and represent a substantial constraint upon the molecular system.

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